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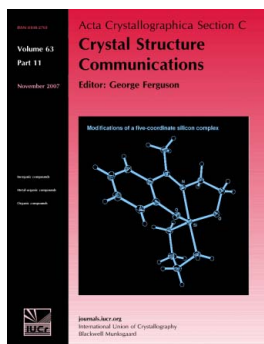
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Strong asymmetric hydrogen bonding in 2-(oxamoylamino)ethylammonium oxamate–oxamic acid (1/1)

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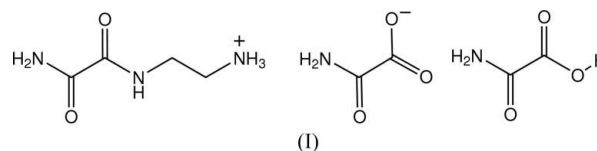
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The title compound, $\text{C}_4\text{H}_{10}\text{N}_3\text{O}_2^+ \cdot \text{C}_2\text{H}_2\text{NO}_3^- \cdot \text{C}_2\text{H}_3\text{NO}_3$, contains at least 11 distinct hydrogen-bond interactions showing a great variety of bond strengths. The shortest and strongest hydrogen bond [$\text{O} \cdots \text{O} = 2.5004(12) \text{ \AA}$] is found between the uncharged oxamic acid molecule and the oxamate monoanion. The grouping formed by such a strong hydrogen bond can thus be considered as a hydrogen bis(oxamate) monoanion. It lacks crystallographic symmetry and the two oxamate groups have different conformations, showing an asymmetric hydrogen-bond interaction. Significantly, the asymmetry allows us to draw a direct comparison of site basicity for the two inequivalent carboxylate O atoms in the planar oxamate anion. The constituent molecular ions of (I) form ribbons, where all amide and carboxylate groups are coplanar. Graph-set analysis of the hydrogen-bonded networks reveals the $R_2^2(10)$ and $R_2^2(9)$ homodromic nets as important structure-directing motifs, which appear to be a common feature of many oxamate-containing compounds.

Comment

Hydrogen bonding is a topic that receives much attention, as it pervades a great many aspects of the world of condensed matter. Hydrogen-bond interactions are crucial in directing structure and subsequent function, from the nature and properties of DNA (Watson & Crick, 1953) to the bizarre polyamorphization of water (Mishima & Stanley, 1998). Taking a materials perspective, there are many ways in which the control of aggregation through hydrogen bonding can be used to advance some specific physical property. Structural assembly can be achieved by using molecules where a particular hydrogen-bond motif is much lower in energy than alternative geometric arrangements (Desiraju, 1995). Such molecules, often dubbed tectons, give a level of predictability to the structures of aggregates. For example, Yang *et al.* (1994)

and Keizer *et al.* (2005) described molecules which self-assemble in solution to form hexameric supramolecular entities. In the solid state, hydrogen-bond interactions that result in discrete adducts can be used to induce mesomorphic behaviour (Bruce & Price, 1994; Willis *et al.*, 1995; Price *et al.*, 1996; Kato *et al.*, 2006), while more extensive interactions can result in predictable extended network structures (Subramanian & Zaworotko, 1994; Coles *et al.*, 2002). Understanding the nature of strong hydrogen bonds is both fundamental to the theoretical understanding of these interactions and useful as a practical tool to engineer specific structural features. One of the strongest hydrogen-bond interactions is that between a carboxylic acid group and a carboxylate anion. Such an interaction occurs in a range of conformations. Most significantly, the observed $\text{C}=\text{O} \cdots \text{O}=\text{C}$ torsion angles range from 0° (*cis*) to 180° (*trans*), and there are many intermediate examples. One important question is how the torsion angle affects the hydrogen-bond potential (Price *et al.*, 2005). Another important question is how the disposition of nearby substituents affects the asymmetry of the hydrogen bond. Usually, the difficulty in answering this question stems from the problem of understanding the contributions of a number of different factors. The title compound, (I), provides a rare and important example where the effects of the geometry of a neighbouring substituent on the hydrogen-bond asymmetry can be rationalized.



Compound (I) consists of three distinct molecular components, *viz.* a 2-(oxamoylamino)ethylammonium cation, an oxamate anion and a neutral molecule of oxamic acid (Fig. 1 and Table 1). Out of the 11 potential hydrogen-bond donors ($\text{N}-\text{H}$ and $\text{O}-\text{H}$), there are at least 11 distinct hydrogen bonds distributed over eight potential acceptor atoms;

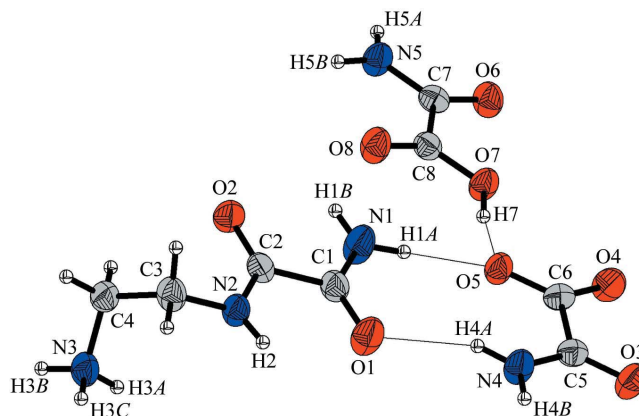
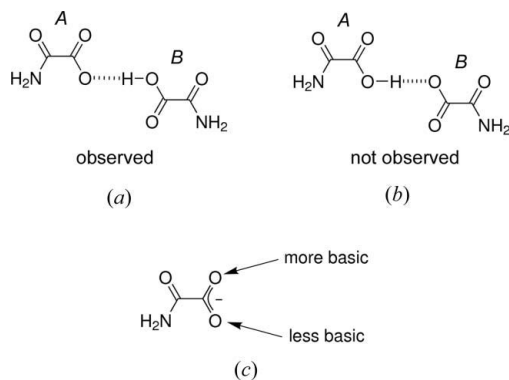


Figure 1
The asymmetric unit of (I), showing the three components and the atom-labelling scheme. Displacement ellipsoids are drawn at the 90% probability level and H atoms are shown as small spheres of arbitrary radii.

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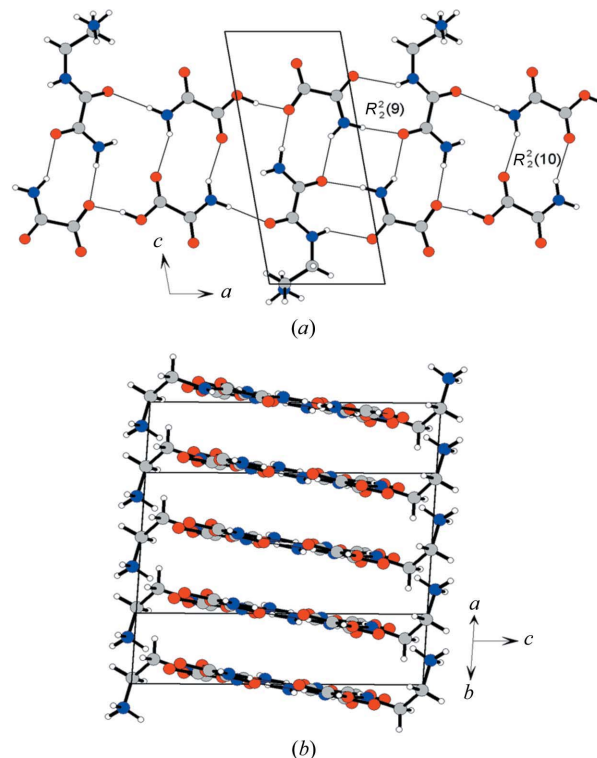
**Figure 2**

(a) The observed and (b) the unobserved possible hydrogen-bonding geometry in the hydrogen bis(oxamate) anion. The different 'conformations' of the oxamate groups are labelled A (with carbonyl O atoms in a *cis* geometry) and B (with carbonyl O atoms in a *trans* geometry). (c) The planar oxamate anion and the relative basicity of the carboxylate O atoms, as inferred from this study.

hydrogen-bond parameters are given in Table 2. The shortest and strongest interaction is the O—H...O ionic hydrogen bond between carboxyl atom O7 and carboxylate atom O5, with O...O = 2.5004 (12) Å. Strong O—H...O hydrogen bonds are defined with O...O separations in the range 2.50–2.65 Å, and very strong hydrogen bonds with O...O < 2.50 Å (Pimentel & McClellan, 1971; Gilli *et al.*, 1994). Thus, in the present case, the hydrogen bond is a strong interaction, and such carboxylate/carboxyl adducts are often considered as distinct structural fragments. Therefore, (I) can be considered as 2-(oxamoylamino)ethylammonium hydrogen bis(oxamate), and is best formulated as $C_4H_{10}N_3O_2^+ \cdot C_4H_5N_2O_6^-$ or $(H_3NCH_2CH_2NHCOCO NH_2)^+ \cdot [(H_2NCOCO)_2H]^-$.

It is well known that as hydrogen bonds become shorter and stronger, the potential will change from an asymmetric shape to a symmetric double-well shape and ultimately to a single symmetric flat-bottomed potential (Emsley, 1980; Perrin & Nielson, 1997). However, environmental factors can have a very significant effect on the nature of the hydrogen-bond potential. Such effects can be seen in all condensed matter states. Perrin (1994) has shown the effect on molecules in different solvents, while Price *et al.* (1995, 1997) have shown changes in the potential as mesomorphic hydrogen-bonded adducts pass through different liquid crystal phases. The solid state is replete with examples where small environmental perturbations affect the hydrogen bond. For example, in the mineral schultenite ($PbHASO_4$), the H atom experiences a double-well potential, and at high temperatures the H atom is positionally disordered over the two sites. On cooling, a broken symmetry and a localization of the H atom to one side are observed, resulting in a ferroelectric phase (Wilson, 1997).

Anionic hydrogen bis(carboxylates) are well known to form strong hydrogen bonds (Price *et al.*, 2005), and in many of these the hydrogen-bond potential is symmetric. However, it is particularly difficult, using X-ray diffraction data, to discriminate single-well from double-well potentials based upon the H-atom position. There is one reported structure that contains the hydrogen bis(oxamate) monoanion (Kovalchukova *et al.*,

**Figure 3**

(a) View of the hydrogen-bonded ribbon that runs in the [310] direction, showing some of the cyclic hydrogen-bond motifs. (b) A view of how the ribbons pack together in the solid state.

2002), where crystallographic symmetry imposes a symmetric potential and, in the reported model, the H atom is located centrally. In (I), the hydrogen bis(oxamate) anion not only lacks any crystallographic symmetry, but is additionally comprised of two oxamate groups with very different conformations (Fig. 2a). Labelled oxamates A and B, these molecules have planar geometries in which the carboxylate carbonyl group is clearly localized. In oxamate A, the C=O and C—O distances are 1.2358 (15) and 1.2726 (15) Å, respectively ($\Delta = 0.037$ Å), and in this fragment the carbonyl O atoms are related by a *cis* geometry. In oxamate B, the C=O and C—O distances are 1.2172 (15) and 1.3015 (15) Å, respectively ($\Delta = 0.084$ Å), and the carbonyl O atoms are in a *trans* geometry. The H atom in this hydrogen bis(oxamate) anion is clearly visible in the Fourier difference map and is located on oxamate B.

The fact that we observe the structure depicted in Fig. 2(a) and not the alternative geometry shown in Fig. 2(b) has interesting implications for the relative basicities of the two distinct carboxylate O atoms in oxamate anion A. Clearly, the O atom *trans* to the NH₂ group of is more basic than the O atom in a *cis* geometry (Fig. 2c). Under solution conditions, where free rotation of the C—C bond occurs, it does not normally make sense to distinguish between these sites, but in rigid solids, and where molecular conformations may be restrained, such a geometric comparison is very useful.

While the anionic hydrogen bis(oxamate) entity contains the shortest and strongest hydrogen bond, we note that in

general the interactions of the amide H atoms are shorter and more linear than those of the cationic ammonium group (Table 2). The stronger amide hydrogen-bond interactions result in a tape-like structure, where all of the oxamide and oxamate groups are approximately coplanar and the peripheral ethylenammonium group adopts a *gauche* conformation (Fig. 3). These ribbons run parallel to the (310) direction, and adjacent ribbons are held together in a three-dimensional net through weaker hydrogen bonds to the ethylenammonium group. Within the ribbon there are seven distinct hydrogen bonds, which together form a number of different motifs. We note the dominance of a first-order $R_2^2(10)$ homodromic motif and two second-order $R_2^2(9)$ homodromic nets (Etter *et al.*, 1990) as significant components of the structure (Fig. 3a). These interactions, along with the related $R_2^2(8)$ motif, have been highlighted by Aakeröy *et al.* (1996) as key hydrogen-bonded patterns in the architecture of oxamide and oxamate salts. A search of the latest version of the Cambridge Structural Database (Version 5.30; Allen, 2002) using *CONQUEST* (Version 1.11; Bruno *et al.*, 2002) reveals the repeated occurrence of these motifs and confirms their importance in determining the network structures of oxamide-containing compounds.

Experimental

Crystals of (I) were obtained as a by-product from a synthesis of ethylenedis(oxamide). Ethylenediamine (1.70 ml, 25.4 mmol) was added slowly to a stirred solution of *O*-ethyl oxamate (10.7 g, 89.7 mmol) in a mixture of water (20 ml) and ethanol (40 ml). The reaction was heated to reflux for 2 h and then allowed to cool to room temperature, whereupon the precipitate of ethylenedis(oxamide) was recovered by filtration. After a few days, crystals of (I) started to grow in the filtrate. IR (attenuated total reflectance, ν , cm^{-1}): 3499, 3418, 3263, 3210, 2991, 2938, 1715, 1627, 1508.

Crystal data

$\text{C}_4\text{H}_{10}\text{N}_3\text{O}_2^+ \cdot \text{C}_2\text{H}_2\text{NO}_3^- \cdot \text{C}_2\text{H}_3\text{NO}_3$	$\gamma = 102.394 (2)^\circ$
$M_r = 309.25$	$V = 623.43 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.1723 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.3560 (4) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$c = 12.1866 (5) \text{ \AA}$	$T = 100 \text{ K}$
$\alpha = 97.765 (2)^\circ$	$0.6 \times 0.1 \times 0.1 \text{ mm}$
$\beta = 97.304 (2)^\circ$	

Data collection

Bruker APEXII CCD area-detector	3812 independent reflections
diffractometer	2895 reflections with $I > 2\sigma(I)$
13083 measured reflections	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.106$	$\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
3812 reflections	
224 parameters	

The ethylene H atoms were placed in idealized geometries, with C—H = 0.97 \AA , and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All other H atoms are involved in hydrogen bonding. While all of these H atoms were located in a difference Fourier map and all had

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C1	1.3208 (15)	C5—O3	1.2381 (15)
C1—O1	1.2330 (15)	C5—C6	1.5542 (17)
C1—C2	1.5353 (17)	C6—O4	1.2358 (15)
C2—O2	1.2353 (15)	C6—O5	1.2726 (15)
C2—N2	1.3297 (15)	N5—C7	1.3331 (16)
N2—C3	1.4634 (16)	C7—O6	1.2303 (15)
C3—C4	1.5135 (17)	C7—C8	1.5406 (16)
C4—N3	1.4918 (16)	C8—O8	1.2172 (15)
N4—C5	1.3207 (16)	C8—O7	1.3015 (15)
O1—C1—N1	124.06 (12)	N4—C5—C6	116.30 (11)
O1—C1—C2	121.19 (11)	O4—C6—O5	127.52 (11)
N1—C1—C2	114.75 (11)	O4—C6—C5	116.40 (11)
O2—C2—N2	125.02 (12)	O5—C6—C5	116.07 (10)
O2—C2—C1	120.66 (10)	O6—C7—N5	125.47 (11)
N2—C2—C1	114.31 (11)	O6—C7—C8	120.73 (11)
C2—N2—C3	121.79 (11)	N5—C7—C8	113.80 (11)
N2—C3—C4	115.14 (10)	O8—C8—O7	126.90 (11)
N3—C4—C3	113.03 (10)	O8—C8—C7	122.18 (11)
O3—C5—N4	124.30 (11)	O7—C8—C7	110.93 (10)
O3—C5—C6	119.40 (11)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O7—H7 \cdots O5	0.96 (2)	1.55 (2)	2.5004 (12)	169.0 (19)
N1—H1A \cdots O5	0.926 (18)	1.941 (18)	2.8665 (15)	178.0 (16)
N1—H1B \cdots O8	0.841 (19)	2.513 (17)	3.0261 (14)	120.3 (15)
N2—H2 \cdots O3 ⁱ	0.838 (16)	2.202 (16)	2.9377 (14)	146.6 (14)
N3—H3C \cdots O4 ⁱⁱ	0.887 (16)	2.018 (17)	2.9027 (14)	175.8 (15)
N3—H3A \cdots O3 ⁱⁱⁱ	0.907 (17)	2.029 (17)	2.8606 (14)	151.7 (14)
N3—H3A \cdots O4 ⁱⁱⁱ	0.907 (17)	2.295 (16)	2.9695 (15)	130.9 (13)
N3—H3B \cdots O7 ⁱⁱ	0.908 (17)	2.305 (16)	2.7828 (14)	112.6 (12)
N3—H3B \cdots O6 ⁱⁱ	0.908 (17)	2.449 (17)	3.1502 (15)	134.2 (12)
N3—H3B \cdots O4 ^{iv}	0.908 (17)	2.639 (16)	3.4143 (15)	143.9 (13)
N4—H4A \cdots O1	0.888 (17)	2.191 (17)	2.9811 (15)	148.0 (14)
N4—H4B \cdots O1 ⁱ	0.888 (17)	1.964 (17)	2.8497 (14)	174.7 (15)
N5—H5A \cdots O2 ^v	0.860 (17)	2.052 (17)	2.9122 (14)	179.4 (16)
N5—H5B \cdots O8 ^v	0.891 (16)	2.181 (17)	3.0172 (15)	156.2 (14)

Symmetry codes: (i) $-x+2, -y+2, -z+1$; (ii) $x, y, z-1$; (iii) $-x+1, -y+2, -z+1$; (iv) $x-1, y, z-1$; (v) $-x-1, -y+1, -z+1$.

their coordinates refined freely, the amide N-bound H atoms had $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. For the H atom in the hydrogen bis(oxamate) unit (H7), the $U_{\text{iso}}(\text{H})$ value was refined freely (geometric parameters given in Table 2).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3064). Services for accessing these data are described at the back of the journal.

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